APPENDIX D

SOIL LEACHING TO GROUNDWATER MODELING

This appendix describes the methods the Montana Department of Environmental Quality (DEQ) used to develop Tier 1 soil leaching to groundwater risk-based screening levels (RBSLs). The soil leaching to groundwater RBSLs were calculated using two computer codes and the EPA soil-water partition equation for organic contaminants (*Soil Screening Guidance Technical Support Document*, EPA, 1996). The EPA partitioning equation was used to relate chemical of concern (COC) concentrations in soil moisture to the total concentration detected in a soil sample, assuming linear partitioning and equilibrium conditions. Dilution/Attenuation Factors (DAFs), representing the ratio of COC concentration in soil leachate at the source area to the COC concentration at the point of compliance (POC), were calculated using the VS2DT Solute Transport in Variably Saturated Porous Media code developed by the USGS. The POC was established as a monitoring well constructed at the downgradient edge of the contaminated source zone, with a well screen extending 1 meter into the water table. The Hydrologic Evaluation of Landfill Performance (HELP) code (U.S. Army Engineer Waterways Experiment Station) was used to generate a generic water budget, including estimates of water infiltration, runoff, evapotranspiration, and soil moisture percolation rates into the contaminated source area. The percolation rates generated by the HELP code were incorporated into the VS2DT modeling.

Physical processes simulated by the DEQ Tier 1 soil leaching to groundwater model include COC adsorption and desorption onto vadose zone soils and the aquifer matrix, advection and hydrodynamic dispersion of COCs in the vadose and saturated zones, and dilution due to mixing of soil leachate and groundwater. The model setup includes a finite contaminant source zone. Biological degradation of the COCs is not considered in the model.

Three scenarios were simulated. In the most conservative scenario, the contaminated source was assumed to be located 0.1 meter above the water table. In the second scenario, the distance between the source and the water table was 3.1 meters. The final scenario incorporated a 6.1-meter layer of unimpacted soil between the source and the water table. WQB-7 human health standards were used as the groundwater target for individual COCs. Groundwater targets for petroleum fractions were developed based on the toxicity and aesthetics of surrogate chemicals representative of each fraction. In all cases, the soil RBSL represents a COC concentration that, based on the results of the modeling effort, would produce a maximum groundwater concentration equal to the groundwater target at the POC.

Generic application of the RBSLs to petroleum release sites throughout Montana dictated the use of several conservative assumptions in the soil leaching to groundwater model. Conservative elements included the use of sandy soil as the default soil type, incorporation of an upper end estimate of the water percolation rate, and the assumption that no biodegradation of COCs in the vadose or saturated zones occurs. A description the VS2DT and HELP codes, model input parameters, and results of the modeling efforts is presented below.

Model Description : VS2DT

VS2DT simulates the movement of water in variably saturated porous media under isothermal and isohaline conditions. The governing equation describing the movement and occurrence of water combines the principle of conservation of mass with equations for fluid flux and storage. A thorough discussion of the derivation of VS2D, the USGS code prior to the addition of a solute transport module, is presented in *Documentation of Computer Program VS2D to Solve the Equations of Fluid Flow in Variably Saturated Porous Media*, USGS, 1987. The code uses finite differences to discretize spatial and temporal domains. Non-linear conductance and storage terms and unsaturated hydraulic conductivities are calculated using equations developed by Brooks and Corey, van Genuchten, or Haverkamp.

The code was modified in 1990 to simulate solute transport, using a governing equation accounting for advective transport, hydrodynamic dispersion, and solute sources and sinks. The hydrodynamic dispersion term includes mechanical dispersion and molecular diffusion in water. The code does not simulate volatilization or COC movement in soil vapor. A discussion regarding the addition of the solute transport module is presented in *Simulation of Solute Transport in Variably Saturated Porous Media With Supplemental Information on Modifications to the U.S. Geological Survey's Computer Program VS2D*, USGS, 1990.

Model Description : HELP

The HELP code was written to simulate water movement through landfills. The model accepts weather, soil, and design data and accounts for surface water and snow storage, snowmelt, runoff, infiltration, evapotranspiration, vegetative growth, soil moisture storage, and unsaturated vertical drainage. The HELP code uses many routines previously developed and used in other hydrologic models, including the WGEN synthetic weather generator (U.S. Department of Agriculture) and Soil Conservation Service (SCS) runoff curves. Snowmelt modeling is based on the National Weather Service River Forecast System Snow Accumulation and Ablation Model, and frozen soils are simulated using a subroutine from the Chemicals, Runoff, and Erosion from Agricultural Management System (CREAMS) code. Vertical drainage is simulated using Darcy's law using unsaturated hydraulic conductivity based on the Brooks and Corey relationship. Results are expressed as daily, monthly, and annual water budgets. Documentations of the HELP Model include the *HELP Model User's Guide for Version 3*, EPA, 1994 and the *HELP Model Engineering Documentation for Version 3*, EPA, 1994.

DEQ Soil Leaching Model Setup

The conceptual model for the soil leaching to groundwater pathway was developed as a two dimensional cross-section consisting of a vadose zone of varying thickness overlying a water table aquifer two meters in thickness. Soil properties were homogeneous and isotropic throughout the model domain. The vertical profile consisted of 1.4 meters of unimpacted soil, overlying 1.5 meters of contaminated soils, overlying a 2 meter saturated zone located 0.1 meter, 3.1 meters, and 6.1 meters below the bottom of the contaminated soils.

The HELP modeling was performed to simulate water movement through the top 1.5-meter layer of soil and generate a soil moisture flux rate for the top boundary of the VS2DT model domain. The HELP code was selected based on its widespread use, flexibility, and thorough documentation. Necessary soil data included porosity, field capacity, wilting point, saturated hydraulic conductivity, initial moisture storage, and SCS runoff curve number. Design specifications included vegetative cover, soil layer thickness and areal dimensions, surface slope and slope length, and evaporative zone depth. Daily precipitation for six Montana cities (Billings, Great Falls, Havre, Helena, Kalispell, and Miles City) was simulated by the HELP code for a 30-year period based on statistical qualities of 5 years of daily field data recorded in these cities. In the same manner, 30 years of synthetic daily temperature and solar radiation data were generated by the code.

The top of the soil column was modeled as bare ground with a surface slope of 1 percent, with 95 percent of the surface area available for runoff. Default soil properties for a well graded sand (soil texture #3) were used in the HELP model. This soil series was selected primarily due to its saturated hydraulic conductivity value, which was approximately one-half the value used in the VS2DT simulation. This reduction in conductivity was included to reflect a moderate degree of compaction expected in surface soils and/or the presence of a semi-permeable cover at many sites. HELP model results indicated that percolation through the bottom of the 1.5-meter layer ranged from 8.3 cm/yr (Kalispell) to 3.8 cm/yr (Helena). HELP model output for Kalispell are presented in Attachment A.

VS2DT Boundary Conditions

The VS2DT model domain was 13 meters in the horizontal direction and 5, 8, and 11 meters in the vertical direction, depending on the depth to groundwater. The top horizontal boundary of the VS2DT model domain was set as a constant flux boundary, and a percolation rate of 2.5×10^{-4} meters per day, corresponding to the Kalispell percolation rate, was used. A water saturated zone was established using constant head boundaries extending 2 meters up from the bottom of the model domain, and were set with a total head difference of 0.06 meters from the left side to the right side of the model domain, resulting in a groundwater gradient of 0.005 m/m. The bottom of the model domain was set 2 meters below and parallel to the water table, and the bottom boundary of the domain and side boundaries of the vadose zone were set as no flow boundaries. The source zone dimensions were set to 9 meters wide (parallel to the groundwater flow direction) and 1.5 meters in thickness. The contaminated source was bordered by two meters of unimpacted soils on each side.

VS2DT Initial Conditions

The VS2DT code requires that initial values of total head, moisture content, or pressure heads be specified everywhere in the model domain. For each distance to groundwater scenario, a preliminary model run was performed to compute an equilibrium pressure head profile for all nodes in the domain based on the boundary conditions and soil textural parameters. The equilibrium pressure head matrices generated by the preliminary runs were subsequently used in the VS2DT simulations for each distance to groundwater scenario. Figure 1 presents the steady-state moisture content profile for the 0.1-meter (most conservative) distance to groundwater scenario.

Unfortunately, the VS2DT code will not accept total COC concentrations in soils as an initial condition. Instead, COC concentrations in soil moisture were set to a constant value (typically 10 g/m^3). An average soil moisture content was calculated for the source zone using the soil moisture profile generated by VS2DT. The total soil concentration in equilibrium with the target soil moisture concentration (back calculated for each COC using the groundwater target multiplied by the DAF) was estimated using the EPA soil-water partitioning equation.

VS2DT Finite Difference Parameters

Rapid changes in pressure heads and moisture content near the capillary fringe dictated relatively fine vertical discretization. Maximum grid spacing in the vertical direction was 0.1 meters in the vadose zone and 0.25 meters in the saturated zone. Minimum grid spacing was 0.01 meters in the vicinity of the water table. Maximum changes in grid spacing ranged from a factor of 1.5 to 2.0. Grid spacing in the horizontal direction was 0.5 meters, and was reduced to 0.25 meters in the vicinity of the compliance monitoring well. Time discretization was set using a maximum time step of 1 day. At the beginning of the simulation, the time step was set to 0.01 day and was subsequently increased by a factor of 1.5 until the 1 day time step was achieved.

Closure criteria for total heads was set to $1.0x10^{-4}$ meters, and closure criteria for the solute transport equation was set to $1.0x10^{-5}$ g/m^3 (g/m^3 units convert to mg/L). The strongly implicit procedure (SIP) was used in calculating total head values, and central differencing in space and time was used for the solute transport equation. The arithmetic mean of adjacent cells was used to calculate intercell conductivities.

Physical and Chemical Parameters

Physical parameters for vadose and saturated zone soils, including hydraulic conductivity, specific storage, porosity, residual moisture content, and van Genuchten non-linear parameters were estimated using the *Subtitle D Landfill Application Manual for the Multimedia Exposure Assessment Model Final Report,* US EPA, 1995. The values selected for these parameters were consistent with a well-sorted sand. Chemical-specific parameters, including the molecular diffusion coefficient in water and the organic carbon-water partitioning coefficient were estimated using the EPA Soil Screening Guidance Technical Support Document. Organic carbon content of vadose and saturated zone soils was estimated as 0.006 g/g and 0.001 g/g, respectively. Longitudinal dispersivity for COCs in the vadose zone was estimated using the equation $D_l = 0.02 + 0.022*L$ where D_l is the longitudinal dispersivity, and L is the vertical distance between the center of the contaminated source area and the top of the water table. For the saturated zone dispersivities, the longitudinal dispersivity was estimated as one tenth the horizontal distance between the center of the contaminated source and the point of compliance monitoring well, and the transverse dispersivity (in the vertical direction) was estimated as one tenth of the value of the longitudinal dispersivity. For the vadose zone, the transverse dispersivity was set equal to the longitudinal dispersivity as the flow of soil moisture perpendicular to bedding planes is expected to result in greater transverse spreading of COCs compared to saturated zone flow parallel to bedding planes. Physical and chemical input parameters incorporated in the leaching to groundwater model are presented in Tables 1 and 2.

Point of Compliance

Conceptually, the point of compliance (POC) was set as a monitoring well constructed at the downgradient edge of the contaminated source with a screened interval extending one meter from the top of the water table. As implemented in the VS2DT code, COC concentrations at five adjacent cell nodes in a vertical line, corresponding to the POC location, were reported for each time step. The uppermost cell was located 10 centimeters below the top of the water table, under the downgradient edge of the vadose zone source. The vertical dimensions of the cells were 0.1, 0.15, 0.25, and 0.25 meters, respectively. In order to generate an average POC well concentration accounting for the differences in cell dimensions, the concentration in each cell was multiplied the cell vertical dimension, the values for all five cells were totalled, and divided by the total vertical length of the five cells (1 meter). This calculation was performed on the output from each time step, and the highest average of the five nodes was recorded. Figures 2 and 3 illustrate the benzene and naphthalene concentrations versus time at the POC well for the 0.1-meter scenario. Figures 4 through 6 present the distribution of benzene at 50 days, 162 days (corresponding to the peak POC concentration), and 500 days for the 0.1-meter distance to groundwater scenario.

The VS2DT input file for the benzene/0.1-meter simulation and schematics illustrating the three scenarios are presented in Attachment B. Model output for this simulation, and the concentration output file for the POC nodes are presented in Attachments C and D.

RBSL Calculation

Back-calculation of RBSLs incorporated the COC-specific DAF generated by the VS2DT modeling and the EPA soil-water partitioning equation. Table 3 presents the EPA partitioning equation and the parameters required for the calculation of the Tier 1 soil targets. DAFs for the most conservative scenario, with the contaminated source located immediately above the water table (0.1-meter scenario), ranged from 20.9 (MTBE) to 12.6 (Fluorene). DAFs for all three scenarios are presented in Table 4 and plotted in Figure 7. Of the PAH compounds, only naphthalene, fluorene, and pyrene were modeled. The majority of the PAHs have very high soil-water partitioning coefficients and correspondingly high retardation factors, resulting in exceedingly long travel times between the source and the POC well. As a result, the DAFs for the PAH COCs were estimated using for DAFs computed for naphthalene and fluorene.

Mass Balance Results

Use of fine spatial and temporal discretization combined with the steady-state flow of soil moisture and groundwater incorporated in the simulations resulted in low water and COC mass balance errors. Table 5 presents mass balance results for MTBE and naphthalene for 0.1-meter and 6.1-meter distance to groundwater scenarios. Percent mass balance for water was calculated as the ratio between the reported fluid volume balance and the total fluid flux. Similarly, the percent mass balance error for the COCs was the ratio between the reported solute mass balance and the initial starting mass. Water and solute mass balances for the shortest simulation (MTBE/ 0.1-meter scenario) were -2.05×10^{-3} cubic meters (0.0098 percent of the total flux) and -0.0126 grams (0.018 percent of the initial mass), respectively. Water and solute mass balances for the longest simulation (naphthalene/6.1-meter distance to groundwater) were -7.55×10^{-3} cubic meters (0.00036 percent of the total flux) and -10.4 grams (0.69 percent of the initial mass), respectively. Figures 8 and 9 present water balance and percent mass balance error results.

All simulations assumed linear COC partitioning between soil and water. The VS2DT code calculates an initial mass of COC sorbed to soil as the initial water concentration multiplied by the partitioning coefficient, soil bulk density, and dimensions of the source area. As Table 5 illustrates, the initial benzene mass in soil moisture was 54 grams , 75 grams were sorbed to the soil, resulting in a total initial mass of 129 grams. Figures 10 and 11 present the total sorbed benzene mass versus time and the rate of benzene desorption versus time for the 0.1-meter simulation.

Sensitivity Analysis Results

Analysis of sensitivity of model output to selected input parameters was performed for the VS2DT and HELP codes. Sensitivity of VS2DT was measured using the benzene/0.1-meter scenario. Sensitivity analysis model runs were performed using expected minimum and maximum values of selected input parameters. Parameter sensitivity was reported as the ratio of predicted POC concentrations for the minimum and maximum case for each input parameter.

Sensitivity results for VS2DT indicated that the benzene/0.1-meter distance to groundwater scenario was most sensitive to the saturated hydraulic conductivity, source width, groundwater gradient, and soil moisture percolation rate. With the exception of the source width, these parameters affect the water balance between percolating soil moisture and the underlying saturated zone. Increasing the saturated zone hydraulic conductivity from 1 meter per day to 15 meters per day resulted in a reduction in the maximum POC concentration by a factor of 5.3. Sensitivity results for the HELP code indicated that simulation was most sensitive to the soil type, site location, and maximum depth of evapotranspiration. Sensitivity analysis results are presented in Table 6 and Figures 12 and 13.

ATTACHMENT A
HELP MODEL OUTPUT

ATTACHMENT B
VS2DT INPUT FILE
AND CONCEPTUAL MODEL SCHEMATICS

ATTACHMENT C
VS2DT OUTPUT FILE

ATTACHMENT D
POC CONCENTRATION FILE